# NOx storage properties of Pt/Ba/Al model catalysts prepared by different methods Beneficial effects of a $N_2$ pre-treatment before hydrothermal aging

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## ARTICLE INFO

## ABSTRACT

The influence of a pre-treatment at 700 °C, either under a $O_2/N_2$ mixture or only under $N_2$, and followed by a hydrothermal aging at 700 °C under wet air, was studied for Pt/Ba/Al NSR model catalysts prepared by different methods: (i) successive impregnation of Ba and Pt, (ii) co-addition of Pt and Ba and (iii) barium precipitation followed by Pt impregnation. The catalysts were evaluated by NOx storage capacity measurements and were characterized by $N_2$ adsorption, XRD, $CO_2$-TPD, $H_2$ chemisorption and $H_2$-TPR. The pre-treatment under $N_2$ largely improves the NOx storage performance in the whole studied temperature range (200–400 °C), with or without $H_2O$ and $CO_2$ in the inlet gas. The better NOx storage properties of the catalysts treated under $N_2$ before aging are due to: (i) a higher NO oxidation activity (mainly linked to a higher platinum dispersion), (ii) a higher number of NOx storage sites resulting from a higher barium dispersion, and consequently to (iii) a higher Pt-Ba proximity.

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## 1. Introduction

Exhaust gases from automotive engines have an important impact on the air quality and consequently on the human health, especially in urban areas with high traffic density. In order to reduce this impact, more and more stringent regulations are imposed to automotive manufacturers. Diesel and direct injection gasoline engines have a potential for improving fuel consumption efficiency and so to reduce $CO_2$ emissions. However, as they operate under an excess of oxygen (lean conditions), it is difficult to reduce nitrogen oxides. A promising solution to overcome this issue was introduced in the mid-1990s by Toyota with the NOx storage-reduction (NSR) concept [1]. NOx traps contain essentially precious metals (Pt, Pd and Rh) for the redox functions and alkaline and/or alkaline earth metals (usually Ba) for the NOx storage function. This system works under transient conditions. During the lean periods, NO is first oxidized into $NO_2$ which is then trapped as nitrite and/or nitrate on the basic storage material. Before unacceptable amounts of NOx slip through the catalyst, the engine switches to rich conditions (excess of hydrocarbons) for a short period where the stored NOx are released and reduced into $N_2$ over the precious metal (Rh).

Model Pt/Ba/$Al_2O_3$ NSR catalysts have been extensively studied during the last 15 years and several mechanisms were proposed for NOx storage-reduction [2]. The first step of the NOx storage, NO oxidation into $NO_2$, takes place mainly on platinum sites. The NO oxidation activity depends on both platinum dispersion and platinum oxidation degree. Putna et al. [3] showed that small platinum particles (about 2 nm) are less active for NO oxidation than larger ones (about 10 nm). This result is explained by the easier formation of platinum oxides on very small particles, platinum oxides being less active for NO oxidation than metallic form. As a result, the activity shows an optimum with the platinum dispersion. The platinum dispersion is strongly influenced by the treatment conditions of the catalysts. As Graham et al. [4] showed, platinum sintering is more marked when the catalyst is treated under $O_2$ and $H_2O$ than without $O_2$ or under $H_2$. Recently, Kim et al. [5] showed that the platinum crystallite size in Pt/Ba/Al catalysts plays a critical role in determining the NOx storage activity. They concluded that the prevention of the platinum sintering is a key factor for the design of durable NOx trap catalysts. Concerning the NOx storage, it is generally admitted that it takes place on multiple types of barium sites which have different activities. Surface barium sites located in platinum proximity are the most active

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[6–11]. Moreover, barium can be present in the catalyst as BaO, $Ba(OH)_2$ and $BaCO_3$, depending on the reaction conditions [12,13]. Lietti et al. [13] have shown that the NOx storage occurs more preferentially on BaO than on $Ba(OH)_2$ and then on $BaCO_3$. However, after exposure to $CO_2$, Ba-containing species were roughly present in the catalyst under two main carbonate forms characterized by their thermal stability: low temperature (LT-$BaCO_3$) and high temperature (HT-$BaCO_3$) species [11]. The LT-$BaCO_3$ species, which correspond to well dispersed species on the alumina support, exhibit a higher activity toward NOx storage-reduction than bulk-like (HT-$BaCO_3$) sites. Thus, one of the main challenges is to improve the barium dispersion in order to obtain the highest NOx storage capacity. Another parameter influences the NOx storage performance: the Pt-Ba proximity. Kabin et al. have shown that the NOx storage takes place in earlier stages mainly on the barium sites located in platinum proximity [14]. A spill-over mechanism involving oxygen and $NO_2$ migration from platinum to barium has been suggested [6,15]. The NOx storage capacity also depends on the temperature, with a volcano like curve. At high temperature (usually $T > 400$ °C), the NOx storage is limited by the stability of adsorbed species, whereas at low temperature (usually $T < 250$ °C), it is limited by the low NO oxidation rate.

We recently reported that barium and platinum dispersions, and thus Pt-Ba proximity of the catalyst and NOx storage properties are influenced by both support oxide and Ba loading [16]. It is expected that these parameters can also be influenced by the preparation method of the catalysts and by the pre-treatment conditions. To our knowledge, only a few studies report the influence of the preparation method [4,5,17–19]. Cant et al. [17] have recently studied the influence of the barium precursor on the NOx storage-reduction properties. They have shown that the use of nitrate or acetate as barium precursor does not significantly influence the NOx storage activity. Dawody et al. [18] also studied the influence of the platinum precursor on the NOx storage properties of Pt/Ba/Al catalysts. The authors have demonstrated that the nitrate precursor led to better properties compared to $H_2Pt(Cl)_6$, $Pt(NH_3)_4(OH)_2$ and $Pt(NH_3)_2(NO_2)_2$. This result was attributed to a higher Pt dispersion. Li et al. have studied the influence of the preparation method of a Pt/Mg/Al catalyst [19]. They found that the impregnation method (Mg and then Pt on alumina) led to better NOx storage properties than the co-precipitation method (Mg + Al and then Pt impregnation). Concerning the thermal treatments, Kim et al. [5] studied the catalyst aging under different atmospheres and observed, in agreement with the results of Graham et al. [4], that the sintering of platinum is less significant when the aging is undertaken under rich conditions. However, information about the barium behavior under different atmospheres is lacking.

Then, the characteristics of an efficient NOx trap catalyst are well known and the aim of this work was to study the influence of the nature of the activation treatment ($N_2$ or $N_2/O_2$) before aging in order to improve Pt and Ba dispersions. The samples are Pt/Ba/Al model catalysts prepared by different methods. The influence of $CO_2$ and $H_2O$ on the NOx storage capacity (rapid NOx uptake) of the different catalysts was systematically investigated to get an in-depth view of catalyst NOx storage performance under realistic conditions.

## 2. Experimental

### 2.1. Catalyst preparation

The $Pt/Ba/Al_2O_3$ catalysts, with 1 wt% Pt and 10 wt% or 20 wt% BaO, were prepared by three different methods. In the first method,

the barium was impregnated on alumina (Axens, 230 $m^2$ $g^{-1}$) from a $Ba(NO_3)_2$ solution. After drying at 120 °C, the material was calcined at 700 °C for 4 h under air. Platinum was then impregnated from a $Pt(NH_3)_2(NO_2)_2$ aqueous solution. This method is named impregnation (noted I). In the second method, the $Ba/Al_2O_3$ material was prepared by the precipitation of barium salt ($Ba(NO_3)_2$) on alumina powder. First, the alumina was added in ultra-pure water and the temperature was raised to 60 °C. After the pH was increased at 10 by adding an ammonia solution, the dry barium salt was added. After drying at 120 °C and calcination at 700 °C for 4 h under air, platinum was then impregnated using the same way as described above. This protocol is named as the precipitation method and is noted (P). In the third method, platinum and barium were successively added without inter-mediate calcination. First, platinum was added into a solution containing the alumina powder at 60 °C. After Pt addition, the barium salt was also added in the same solution. The catalyst was then dried at 120 °C. This method is called co-addition and noted CA.

After drying, the different catalysts were pre-treated at 700 °C for 4 h under a mixture containing 10% $O_2$ balanced in $N_2$, or only $N_2$. Finally, the catalysts were aged at 700 °C for 4 h under a mixture containing 10% $O_2$, 5% $H_2O$ and $N_2$, and cooled down under the same mixture until 100 °C. The catalysts are noted Pt/xBa/Al where x is 10 or 20 wt% BaO.

It is important to note that the catalysts may evolve during long storage at room temperature. Particularly, a growing of bulk $BaCO_3$ can be observed. As a consequence, all the tests presented in this study were performed using the same procedure, i.e. with the same delay between the catalyst preparation and the consecutive tests and characterizations. Only the delay for the XRD experiment was not rigorously controlled, and the data were used accordingly.

### 2.2. NOx storage capacity measurements

Before the NOx storage capacity measurements, the catalyst (60 mg) was pre-treated at 550 °C for 30 min under a 10% $O_2$ and $N_2$ mixture (total flow rate: 10 L $h^{-1}$), and then cooled down to the storage temperature under the same mixture. The sample was then submitted to a 350 ppm NO, 10% $O_2$ and $N_2$ mixture (total flow rate: 10 L $h^{-1}$) at 200, 300 or 400 °C. Effect of water and carbon dioxide was also studied. In this case, 10% $H_2O$ and 10% $CO_2$ were added in both pre-treatment and measurement mixtures. The gas flow was introduced using mass-flow controllers (Brooks), except for $H_2O$ which was introduced using a thermostated saturator. Both NO and NOx concentrations (NO + $NO_2$) were followed by chemiluminescence with a COSMA Topaze 2020 apparatus. $H_2O$ was removed prior to NOx analysis with a membrane dryer. The NOx storage capacity was estimated by the integration of the recorded profile for the first 100 s after subtraction of the contribution of the apparatus (dead volume) deduced from a test without catalyst. The platinum oxidation activity was estimated as the $NO_2$/NOx ratio (%) at saturation (usually about 900 s). Under the conditions used in the NOx storage measurements (60 mg, 10 L $h^{-1}$, 350 ppm NO), 67 $\mu$mol NOx per gram of catalyst are injected in 100 s.

### 2.3. Catalyst characterizations

#### 2.3.1. Nitrogen adsorption, XRD, and TEM
$N_2$ adsorption was carried out at −196 °C with a Tristar 3000 Micromeritics apparatus. Prior to the measurements, the samples were pre-treated at 350 °C under vacuum for 12 h in order to eliminate the adsorbed species. The specific surface areas were calculated using the BET method.

X-ray powder diffraction was performed at room temperature with a Siemens D5005 Bragg–Brentano ($\theta$–$\theta$) apparatus using a Cu K$\alpha$ radiation ($\lambda = 0.154056$ nm). The diffractogramms were recorded with a step of 0.02° $2\theta$, with a dwell time of 2 s. The powder was deposited on a silicium wafer. The crystalline phases were identified by comparison with the ICDD database files.

Transmission electron microscopy (TEM) images were obtained with a Philips CM 120 microscope operating at 120 kV, equipped with an energy-dispersive X-ray detector (EDX).

### 2.3.2. Hydrogen chemisorption

The noble metal dispersion of Pt-containing catalysts was determined using the $H_2$ chemisorption method. The catalyst was first reduced under pure hydrogen at 500 °C for 1 h and then flushed at the same temperature under argon for 3 h. The reactor was cooled under argon at room temperature, where hydrogen was dosed on the sample until saturation. After flushing under argon for 10 min, the sample was exposed to hydrogen again. The amount of chemisorbed hydrogen was taken as the difference between the two hydrogen exposures.

### 2.3.3. $CO_2$ thermodesorption

Prior experiments, the catalyst was pre-treated at 550 °C for 30 min under a 1% $O_2$/He flow and cooled down to 50 °C. This temperature was chosen after IRTF and XRD experiments [16] in order to decompose only surface $BaCO_3$, without $BaCO_3$ bulk decomposition. The adsorption of $CO_2$ was carried out for 1 h at this temperature. After flushing under a 1% $O_2$/He mixture at 50 °C to remove the physisorbed species, the $CO_2$ temperature programmed desorption (TPD) was followed from 50 °C up to 700 °C by thermal conductivity.

### 2.3.4. Temperature programmed reduction (TPR) of sulfated catalysts

In the sulfation process, the catalyst was exposed to a 100 ppm $SO_2$, 10% $CO_2$, 10% $O_2$, 10% $H_2O$ and $N_2$ mixture at 300 °C for 5 h. If all the sulfur is deposited on the catalyst, a maximum of 2 wt% S is obtained. After flushing at 300 °C under 10% $CO_2$, 10% $O_2$, 10% $H_2O$ and $N_2$ mixture for 15 min, the sample was cooled down to room temperature under the same mixture except for water which was removed from the flow at 100 °C.

Prior to the TPR test, the sulfated catalyst (65 mg) was first pre-treated in situ under oxygen at 300 °C for 30 min and cooled to room temperature. After flushing under argon for 45 min, the reduction was carried out from room temperature up to 800 °C under a 1% $H_2$/Ar mixture, using a 5 °C min$^{-1}$ heating rate. The

sample was maintained at 800 °C for 30 min before cooling under argon. Hydrogen consumption was followed by thermal conductivity.

Some experiments were also carried out on unsulfated catalysts to study the platinum reduction. In this case, 500 mg of hydrothermally aged catalyst were used and the in situ pre-treatment was carried out at 550 °C under $O_2$.

## 3. Results and discussion

### 3.1. NOx storage capacity measurements

#### 3.1.1. NOx storage capacity in the absence of $H_2O$ and $CO_2$

Fig. 1 reports the NOx storage capacities measured for the first 100 s (rapid NOx uptake) in the absence of $H_2O$ and $CO_2$ in the inlet mixture. Generally, the catalyst preparation method (I, P or CA) has only a weak effect on the NOx storage capacity, whatever the storage temperature, the barium loading, and the pre-treatment before aging. Only the CA method leads to a slight improvement of the NOx storage capacities when the catalysts were treated under $O_2$/$N_2$ before aging. However, this behavior is no longer observed when the catalysts are treated at 700 °C under $N_2$. These results seem to contradict those recently obtained by Li et al. [19] who showed that the impregnation method led to a higher NOx storage capacity than the precipitation one for a Pt/Mg/Al catalyst. It can be explained by the co-precipitation method of Al and Mg which led to a very low surface area: 42 m$^2$ g$^{-1}$ versus 142 m$^2$ g$^{-1}$ for the impregnation method. In our study, barium is precipitated on an alumina powder of 230 m$^2$ g$^{-1}$. Then, the preparation method has no significant impact on the surface area of our catalysts (Table 1).

In opposition to the preparation method, the NOx storage performances are strongly influenced by the pre-treatment atmosphere before aging. Fig. 1 shows that the $N_2$ pre-treated catalysts exhibit higher NOx storage capacities whatever the barium loading, the barium deposition method and the temperature test. For the different Pt/10Ba/Al catalysts (Fig. 1a), the $N_2$ pre-treatment led to an increase of the NOx storage capacity by an average factor of 1.36. The improvement is even more significant for the 20% BaO catalysts (factor of 1.74), leading to a maximum value of 55 $\mu$mol g$^{-1}$ at 400 °C (Fig. 1b).

It can be also noted in Fig. 1 that the NOx storage capacities of the 10% BaO loaded catalysts are generally not influenced by the temperature of the experiment. In opposition, the NOx storage capacities of the 20% BaO loaded catalysts increase with the temperature test. This can be attributed to a stronger basic
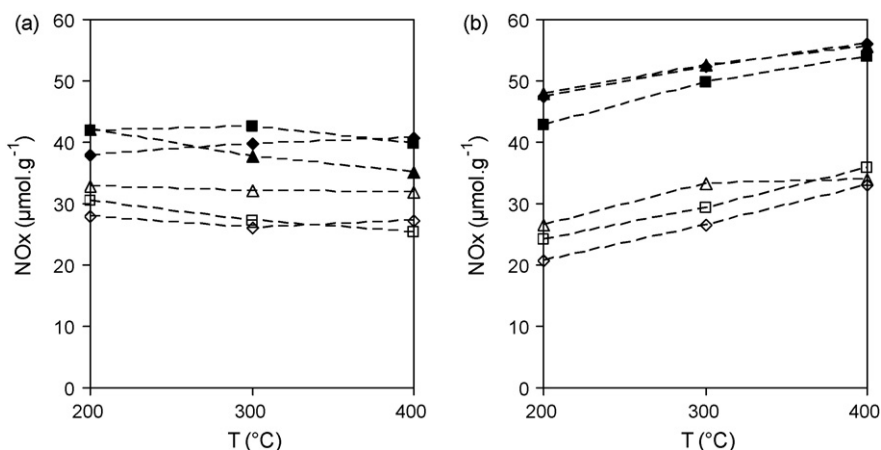


**Fig. 1.** NOx storage capacity for the first 100 s vs. temperature of aged (a) Pt/10Ba/Al and (b) Pt/20Ba/Al catalysts pre-treated under $O_2$/$N_2$ (blank symbols) or $N_2$ (solid symbols). ($\Diamond$, $\blacklozenge$) Impregnation method, ($\square$, $\blacksquare$) precipitation method and ($\triangle$, $\blacktriangle$) co-addition method. Feed gas: 10% $O_2$, 350 ppm NO and $N_2$.

**Table 1**
BET surface area, pores volume ($V_p$) and main phases detected by XRD for alumina and Ba/Al materials with 10 and 20 wt% BaO after calcination at 700 °C

| Material | $Al_2O_3$ | 10 wt% BaO | | 20 wt% BaO | |
|---|---|---|---|---|---|
| | | I | P | I | P |
| BET ($m^2\,g^{-1}$) | 218 | 173 | 172 | 122 | 136 |
| $V_p$ ($cm^3\,g^{-1}$) | 0.46 | 0.44 | 0.42 | 0.35 | 0.35 |
| Main phases detected by XRD | | $BaAl_2O_4$ | | $BaAl_2O_4$ | |

I, Impregnation method; P, precipitation method.

strength for the 20% BaO loaded catalysts [16]. As large Ba particles exhibit a higher basic strength than well dispersed barium particles [16], it induces that the barium dispersion should be higher for the 10% BaO loaded catalysts compared to the 20% BaO loaded catalysts. This idea is further developed in the "catalysts characterizations" part.

In order to know if the $N_2$ pre-treatment contributes to the increase of the total number of storage sites or just improve the rapid storage, the NOx storage capacity was then calculated after 900 s. Results are reported in Fig. 2. The NOx storage saturation is generally obtained at this time under the experimental conditions used in the present work. Fig. 2 shows that the number of available NOx storage sites depends on both the preparation method and the pre-treatment of the catalyst before aging. In comparison with the $O_2/N_2$ pre-treatment, the $N_2$ pre-treatment effectively leads to an increase of the total number of storage sites whatever the preparation method. Moreover, in this case, the NOx storage curves exhibit a maximum at 300 °C which can be attributed to a lower proportion of strong basic sites, and therefore to a higher barium dipersion [16]. This hypothesis will be discussed further in the text. For the 10% BaO catalysts, the higher performances are observed with the co-addition method, while the impregnation one leads to the worst storage properties whatever the pre-treatment. The reverse behavior is observed for the 20% BaO catalysts.

The NOx storage capacity can also depend on the NO oxidation activity since it was established that the oxidation activity is the limiting step mainly at low temperature, whereas at higher temperature, the NOx storage is limited rather by the nitrates stability [2]. Nevertheless, a higher oxidation activity would also lead to an increase of the nitrates stability due to the increase of the partial pressure of $NO_2$, thus shifting the decomposition temperature of nitrates [20].
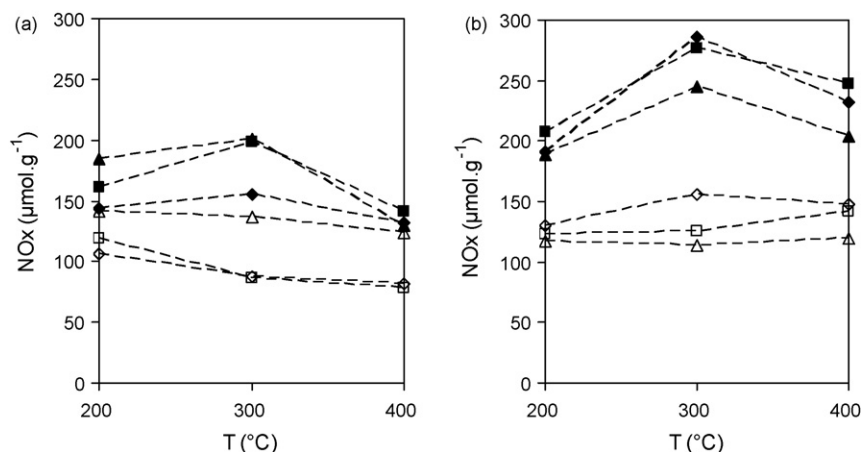
As Fig. 3 shows, the NO oxidation activity, estimated at saturation (900 s) by the $NO_2/NOx$ ratio (%), is also significantly improved by the $N_2$ pre-treatment. Compared to the $O_2/N_2$ pre-treatment, the $NO_2/NOx$ ratio increases by an average factor of 2 at 200 and 300 °C, and 1.4 at 400 °C. Thus, the improvement of the NO oxidation activity should also contribute to the increase of the rapid NOx storage in the 200–400 °C temperature range (Fig. 1).

As previously suggested, the higher performance of the $N_2$ pre-treated catalysts can be also linked to a higher barium dispersion. Piacentini et al. [11] showed the existence of various types of barium species with different NOx storage activities in the absence of $H_2O$ and $CO_2$. The most active sites are the well dispersed barium particles. Their results are supported by those of Gangwal et al. [21] who proposed two different barium sites, semi-bulk and bulk species. The latter authors also showed that the NOx trapping occurs first on semi-bulk species whereas the bulk sites are active only in the later stage of trapping. We also reported in a recent paper [16] that, in the presence of water and carbon dioxide, an increase in barium dispersion led to a higher NOx storage capacity and to a decrease of the inhibiting effect of $CO_2$. So, in order to examine if the nitrogen pre-treatment has an influence on the barium dispersion, the influence of $H_2O$ and $CO_2$ on the rapid NOx storage (100 s) was further investigated.

### 3.1.2. NOx storage capacity measured in presence of $H_2O$ and $CO_2$ in the inlet gas

The NOx storage capacities measured for the first 100 s in presence of $CO_2$ and $H_2O$ are reported in Fig. 4. The presence of water is known to affect the oxidation activity of the catalysts, leading to a decrease of NO oxidation activity of Pt. Concerning $CO_2$, it competes with NOx for the adsorption on the storage sites. The more the basic strength of the storage sites is high, the more the carbon dioxide competes [2,16,22].

The loss of the NOx storage capacity (%) due to the presence of $H_2O$ and $CO_2$ is near 50–60% for the $O_2/N_2$ pre-treated catalysts and lower than 40% for the $N_2$ pre-treated catalysts before aging. These results suggest that the nitrogen pre-treatment leads to a higher barium dispersion, since $CO_2$ has a lower inhibiting effect on the NOx storage capacity. Finally, the differences of NOx storage capacities between the two pre-treatments are even more significant in the presence of $H_2O$ and $CO_2$. Thus, the $N_2$ pre-treated catalysts exhibit NOx storage capacities more than two times higher than the $O_2/N_2$ pre-treated catalysts. In fact, the average increase factor is 2.0 and 2.4 for the 10% BaO and 20% BaO contents, respectively. This beneficial effect is attributed to both a
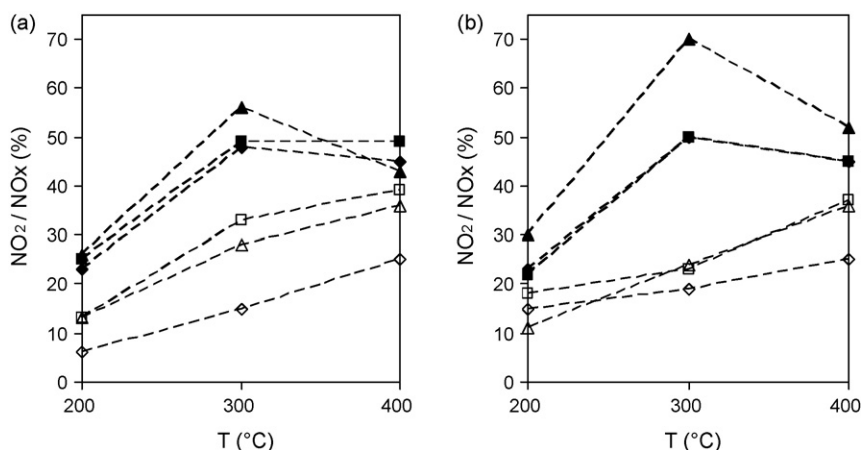


**Fig. 2.** NOx storage capacity at 900 s vs. temperature of aged (a) Pt/10Ba/Al and (b) Pt/20Ba/Al catalysts pre-treated under $O_2/N_2$ (blank symbols) or $N_2$ (solid symbols). ($\diamond$, $\blacklozenge$) Impregnation method, ($\square$, $\blacksquare$) precipitation method, and ($\triangle$, $\blacktriangle$) co-addition method. Feed gas: 10% $O_2$, 350 ppm NO and $N_2$.

**Fig. 3.** NO$_2$/NOx ratio (%) determined at saturation (900 s) vs. temperature of aged (a) Pt/10Ba/Al and (b) Pt/20Ba/Al catalysts pre-treated under O$_2$/N$_2$ (blank symbols) or N$_2$ (solid symbols). ($\diamond$, $\blacklozenge$) Impregnation method, ($\square$, $\blacksquare$) precipitation method, and ($\triangle$, $\blacktriangle$) co-addition method. Feed gas 10% O$_2$, 350 ppm NO and N$_2$.
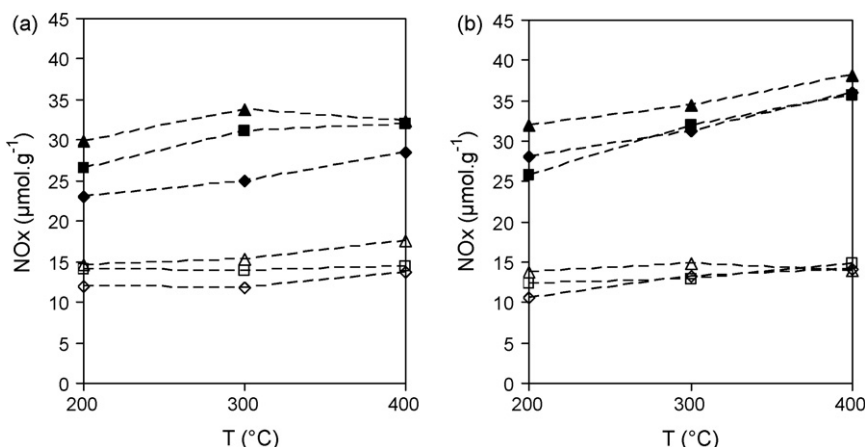


**Fig. 4.** NOx storage capacity for the first 100 s vs. temperature of aged (a) Pt/10Ba/Al and (b) Pt/20Ba/Al catalysts pre-treated under O$_2$/N$_2$ (blank symbols) or N$_2$ (solid symbols). ($\diamond$, $\blacklozenge$) Impregnation method, ($\square$, $\blacksquare$) precipitation method, and ($\triangle$, $\blacktriangle$) co-addition method. Feed gas: 10% O$_2$, 350 ppm NO, 10% H$_2$O, 10% CO$_2$ and N$_2$.

higher activity for the NOx storage and a lesser inhibiting effect of H$_2$O and CO$_2$. Fig. 4 also shows that the catalysts prepared by the impregnation method present the lower NOx storage capacities and the higher inhibiting effect of CO$_2$ and H$_2$O, indicating that the impregnation method leads to a lower barium dispersion.

Otherwise, in the presence of CO$_2$ and H$_2$O, barium loading has nearly no significant influence on the NOx storage capacity (Fig. 4). These results are in agreement with those reported in a recent paper [16], and are attributed to an increase of the inhibiting effect of CO$_2$ and H$_2$O with the barium loading due to an increase of the basicity of the catalysts.

Besides, some additional tests were performed in order to show if the beneficial impact of the N$_2$ pre-treatment remains after sulfur poisoning and sulfur regeneration of the hydro-thermally aged catalysts. It was previously shown that for Pt/Ba/Al catalysts without N$_2$ pre-treatment, the initial NOx storage capacity was recovered after regeneration [23]. Then, some similar tests were performed on the aged Pt/xBa/Al samples prepared by precipitation and pre-treated under N$_2$. The catalysts were sulfated at 300 °C following the protocol detailed in Section 2 for the H$_2$-TPR of sulfated catalysts. For the regeneration of the sulfated catalysts, the samples were submitted to a 2.5% H$_2$, 10% CO$_2$, 10% H$_2$O and N$_2$ mixture at 550 °C for 30 min [23]. The NOx storage measurements were carried out at 300 °C with H$_2$O and CO$_2$ in the feed stream and the results are presented in Table 2. As expected, the sulfating treatment led to a strong decrease of the NOx storage capacity,

with a loss of more than 50%. However, the NOx storage capacity is completely recovered after the regeneration step, indicating that N$_2$ pre-treatment effect still exists after sulfur poisoning and consecutive treatment in rich atmosphere.

In order to confirm the previous conclusions about the influence of the pre-treatment atmosphere on the physico-chemical properties of the catalysts, the samples were then characterized by nitrogen adsorption, XRD, H$_2$ chimisorption, TEM coupled to EDX analysis, CO$_2$-TPD and H$_2$-TPR.

### 3.2. Catalysts characterizations

In this section, all the characterizations of catalysts were performed on the hydrothermally aged samples at 700 °C, excepted for the material without platinum.

**Table 2**
NOx storage capacity (100 s) at 300 °C in presence of H$_2$O and CO$_2$ for the aged Pt/xBa/Al samples prepared by precipitation method and pre-treated at 700 °C under N$_2$ before aging (influence of sulfur poisoning and sulfur regeneration)

|  | Pt/10Ba/Al | Pt/20Ba/Al |
|---|---|---|
| Aged catalyst ($\mu$mol g$^{-1}$) | 31.2 | 31.9 |
| Sulfated catalyst ($\mu$mol g$^{-1}$) | 13.2 | 14.9 |
| Regenerated catalyst ($\mu$mol g$^{-1}$) | 29.7 | 30.9 |
| Recovered (%) | 95 | 97 |

### 3.2.1. Nitrogen adsorption and XRD

The surface area and pore volume ($V_p$) of the different materials after barium deposition and calcination at 700 °C are reported in Table 1. For comparison, the BET surface area of the alumina powder after calcination at the same temperature is also reported. Table 1 shows that the deposition method has no significant effect on the surface area and pore volume at this catalyst preparation stage. However, note that the higher is the barium loading, the lower are the surface area and pore volume. Also, after barium deposition and calcination at 700 °C, the main crystalline phase detected by XRD was $BaAl_2O_4$ whatever the barium deposition method (results not shown). As the method of barium deposition has practically no effect on the structure and the surface area, only the catalysts with 10 and 20 wt% BaO prepared by the impregnation (I) method were characterized after platinum deposition and subsequent thermal treatments ($N_2$ or $O_2/N_2$ pre-treatment at 700 °C followed by the hydrothermal aging at 700 °C).

Table 3 reports the BET surface area, the pore volume ($V_p$) and the main XRD phases obtained with the aged Pt/$x$Ba/Al catalysts prepared by the precipitation method. Table 3 shows that the catalyst pre-treatment under $N_2$ or $O_2/N_2$ has significant influence neither on the surface area nor on the nature of the crystalline phases detected by XRD ($BaAl_2O_4$ and $BaCO_3$). However, some phase transformation occurred during the platinum addition. Indeed, the XRD pattern of the obtained sample after drying at 120 °C (without consecutive calcinations) does not exhibit the characteristic ray of $BaAl_2O_4$ anymore. Then, it was concluded that barium was leaching from the support [24,25]. The barium carbonate formation can occur early in solution by reaction with the dissolved $CO_2$ coming from air. However, this species should disappear during the thermal treatment at 700 °C, leading also to the formation of new $BaAl_2O_4$. More probably, the observed $BaCO_3$ is coming from reaction with $CO_2$ during air exposure.

The surface area measurements and XRD analysis do not allow one to explain the influence of the pre-treatment atmosphere on the NOx storage behavior. These results seem to indicate that the catalyst pre-treatment influences mainly the surface structure of the catalyst and not its structural and textural properties. Thus, next we focus on the characterization of the surface sites.

### 3.2.2. Platinum accessibility

The $H_2$ chemisorption measurements were carried out as mentioned above in the experimental part. Only the aged Pt/20Ba/Al catalysts prepared by the precipitation method were studied. Platinum dispersion was of 4% for the catalyst pre-treated under $O_2/N_2$ before aging, and 8% for the nitrogen pre-treated catalyst. The higher platinum dispersion can be explained by the nature of the pre-treatment gas. Graham et al. [4] showed that platinum sintering strongly depends on the atmosphere of the thermal treatment. Thus, platinum sintering is lower when the catalyst was treated without oxygen in the gas feed. Nevertheless, note that in our study, the catalysts were aged at 700 °C under a $O_2/H_2O/N_2$ mixture for 4 h after the pre-treatment. Thus, the nitrogen

treatment contributes to maintain a higher dispersion of platinum even after the thermal aging.

Another parameter which can be influenced by the nature of the pre-treatment mixture is the oxidation state of platinum. A treatment under inert or reducing conditions would lead to a higher reduction state of platinum particles, while a treatment under $O_2$ should maintain the platinum particles in a more oxidized state. To corroborate this assumption, the oxidation state of the platinum has been evaluated by $H_2$-TPR.

### 3.2.3. Temperature programmed reduction

Before measurement, the aged catalysts were treated at 550 °C under oxygen in the TPR apparatus. Only the aged Pt/20Ba/Al catalysts, previously treated under $O_2/N_2$ or $N_2$ before aging, were tested. The TPR profiles show a reduction peak at about 150 °C (results not shown), which corresponds to the reduction of the platinum oxides. Nevertheless, the $H_2$ consumption depends on the catalyst pre-treatment. It increases from 30 to 39 $\mu$mol $g^{-1}$ for the $N_2$ and $N_2/O_2$ pre-treatments, respectively. These results indicate that the platinum is in a more reduced state for the nitrogen pre-treated catalyst. As metallic platinum is more active than platinum oxide for NO oxidation, this result can partially explain the higher NO oxidation activity of the $N_2$ pre-treated catalysts.

To summarize, the nitrogen pre-treatment contributes to maintain not only a higher dispersion of platinum but also a higher reduction degree of platinum. These two effects lead to the higher NO oxidation activity previously observed (Fig. 3) and thus contribute to higher NOx storage properties.

### 3.2.4. Transmission electron microscopy

The Pt/20Ba/Al catalysts prepared by precipitation were characterized by TEM coupled to an EDX analysis. This study was performed on the aged samples pre-treated at 700 °C either under $N_2$ or $O_2/N_2$. Representative micrographs of the catalysts are reported in Fig. 5. The TEM analysis of numerous pictures indicates that the mean platinum particle size is about 20 nm for the $O_2/N_2$ pre-treated catalyst and 12 nm for the $N_2$ one, corresponding to platinum dispersions of approximately 5 and 9%, respectively (Fig. 5a and b). These results are in good agreement with those obtained by $H_2$ chemisorption. For both catalysts, the TEM analysis also shows the presence of two types of zones, clear (Fig. 5c) and dark ones (Fig. 5d). The EDX analysis of dark areas always showed the presence of Pt, Ba and Al for both catalysts. Concerning the clear areas, the EDX analysis showed that only Al was generally detected for the catalysts pre-treated under $O_2/N_2$, whereas Pt, Ba, and Al were generally detected for the catalysts pre-treated under $N_2$. These results indicate that the nitrogen pre-treatment before thermal aging at 700 °C contributes not only to maintain a higher platinum dispersion, but also a higher barium dispersion. In order to confirm if the barium dispersion is really affected by the pre-treatment atmosphere, some $CO_2$ thermodesorption experiments were performed.

**Table 3**
BET surface area, pores volume ($V_p$) and main phases detected by XRD for the Pt/$x$Ba/Al catalysts after hydrothermal treatment

| Aged catalysts | Pt/10Ba/Al | | Pt/20Ba/Al | |
|---|---|---|---|---|
| | 700 °C, $N_2$[a] | 700 °C, $N_2 + O_2$[a] | 700 °C, $N_2$[a] | 700 °C, $N_2 + O_2$[a] |
| $S_{BET}$ (m$^2$ g$^{-1}$) | 175 | 162 | 136 | 130 |
| $V_p$ (cm$^2$ g$^{-1}$) | 0.46 | 0.42 | 0.36 | 0.38 |
| Main phases detected by XRD | | $BaAl_2O_4$, $BaCO_3$ | | $BaAl_2O_4$, $BaCO_3$ |

Barium was deposited by the impregnation method.
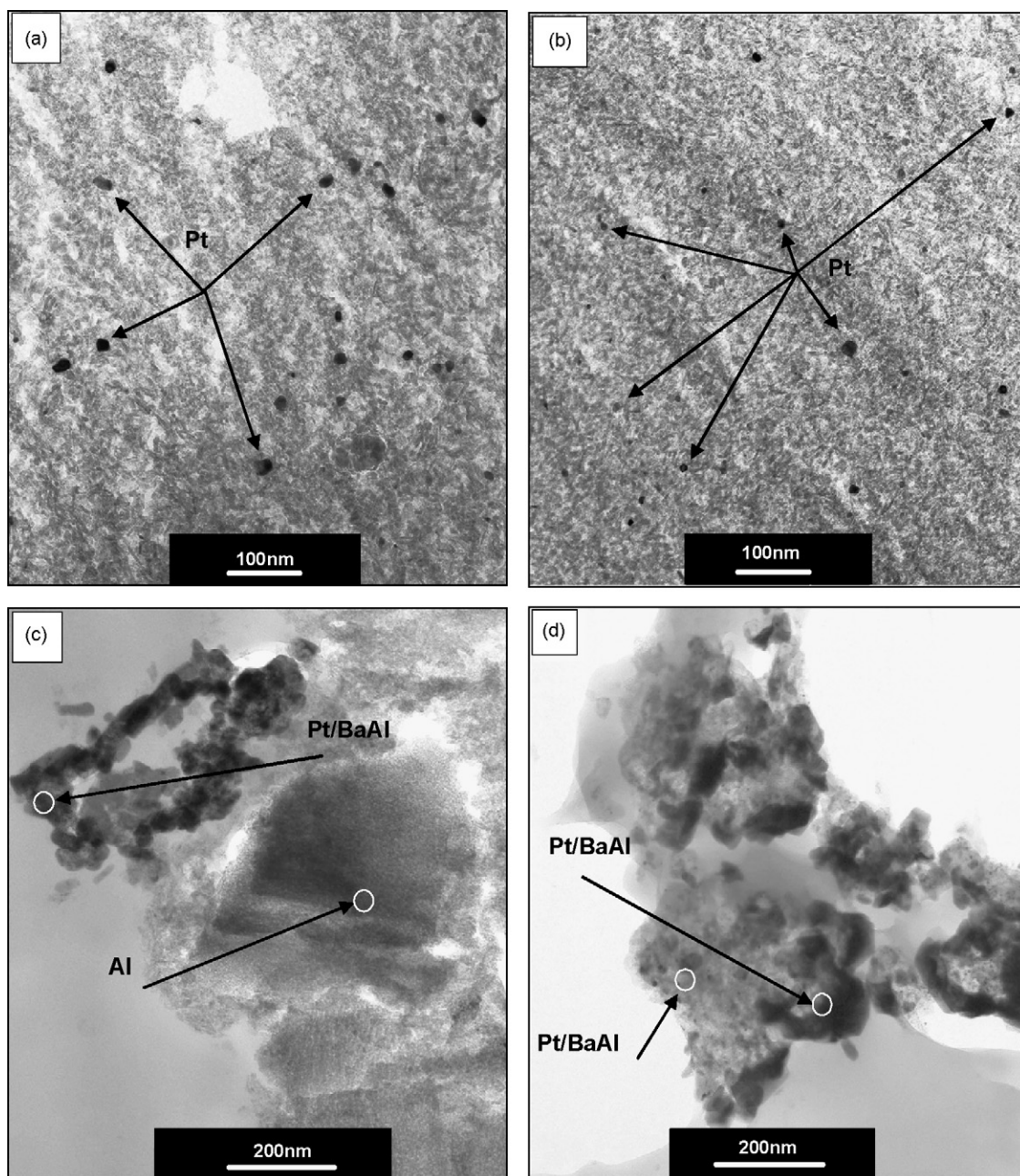[a] Pre-treatment before aging.

**Fig. 5.** Micrographs of the aged Pt/20Ba/Al catalysts prepared by precipitation method and pre-treated either under (a and c) $O_2/N_2$ or (b and d) under $N_2$.

### 3.2.5. Carbon dioxide thermodesorption ($CO_2$-TPD)

The aged Pt/10Ba/Al and Pt/20Ba/Al catalysts prepared by the precipitation method were selected for this study. The catalysts were previously exposed to ambient air for the same time period in order to obtain a similar carbonatation degree. Prior to the TPD experiments, the aged catalysts were treated at 550 °C under 1% $O_2$/He and $CO_2$ was then adsorbed at 50 °C. The TPD profiles are presented in Fig. 6 and exhibit two main peaks near 100 and 650 °C.

We reported in a recent paper that the peak near 650 °C corresponds to the decomposition of bulk $BaCO_3$ formed on the catalysts during the preparation and the air exposure. Concerning the $CO_2$ desorption in the 50–550 °C temperature range, it corresponds to the adsorption on the surface basic sites [16]. Fig. 6 shows that the peak at high temperature (650 °C) is more intense for the $O_2/N_2$ pre-treated catalysts compared with the $N_2$ one, whatever the barium loading. These results suggest that, for

the same barium loading, the amount of bulk barium carbonates is higher for the $O_2/N_2$ pre-treated catalysts, pointing out a lower dispersion of barium. On the other hand, the catalysts pre-treated under $N_2$ show a higher $CO_2$ desorption in the 50–550 °C temperature range, indicating a higher number of surface basic sites. This result is in accordance with the total NOx storage capacitiy measured at 900 s (Fig. 2).

Thus, the results of $H_2$ chemisorption, TEM coupled with EDX analysis and $CO_2$-TPD show that the nitrogen pre-treatment before aging contributes to maintain higher platinum and barium dispersions. As a consequence, the Pt-Ba proximity would be also increased. A good Pt-Ba proximity is required to achieve high NOx trapping performance due to the spill-over of $NO_2$ species from platinum to barium sites, especially for the rapid NOx storage [14]. This Pt-Ba proximity parameter can be evaluated by $H_2$-TPR experiments of sulfated catalysts.
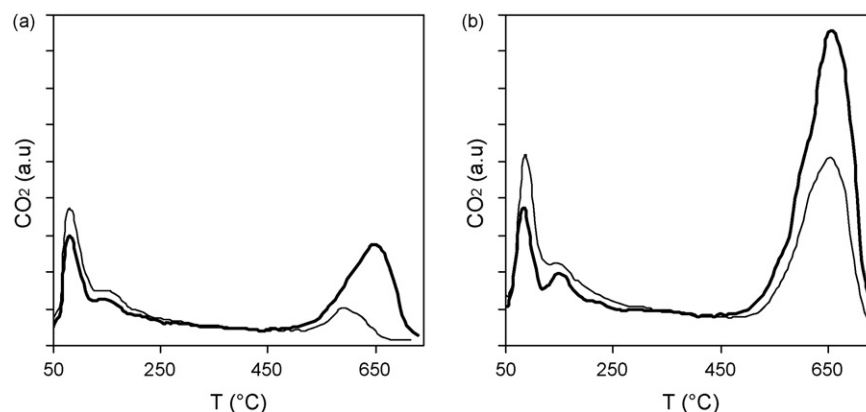
**Fig. 6.** $CO_2$-TPD profiles of aged (a) Pt/10Ba/Al and (b) Pt/20Ba/Al catalysts prepared by precipitation method, and pre-treated either (−) under $N_2$ or (▬) under $O_2/N_2$.

### 3.2.6. Temperature programmed reduction under hydrogen (H₂-TPR) of sulfated catalysts

As reported in the literature, sulfate stability is strongly influenced by barium dispersion and Pt-Ba proximity [23,26]. Indeed, the sulfates formed on well dispersed barium particles in platinum proximity and the surface sulfates are less stable than bulk barium sulfates. In this way, the TPR profiles of sulfated catalysts can give information about the Pt-Ba proximity and Ba dispersion. This study was carried out over the aged Pt/20Ba/Al catalysts prepared by impregnation, precipitation and co-addition. To perform these experiments, the catalysts were first sulfated at 300 °C in oxidizing atmosphere. The TPR profiles of sulfated Pt/20Ba/Al are reported in Fig. 7. Concerning the $N_2$ pre-treated catalysts, three main reduction peaks are observed at about 500, 600 and 750 °C. According to a recent study [23], the peak at 500 °C is ascribed mainly to the reduction of the well dispersed barium sulfates located in platinum proximity, with a small contribution of the aluminum sulfates reduction. The second peak is attributed to the reduction of more crystallized surface barium sulfates, more or less located in Pt neighboring.

Finally, the third one is ascribed to the reduction of bulk barium sulfates.

Concerning the sulfated catalysts pre-treated under $O_2/N_2$, only two reduction peaks were observed, near 650 and 750 °C (Fig. 7). Firstly, the $O_2/N_2$ pre-treatment leads to an increase of the $H_2$ consumption attributed to the bulk $BaSO_4$ reduction (peak near 750 °C) compared to the $N_2$ pre-treatment. This is in accordance with a higher barium dispersion after the $N_2$ pre-treatment, as previously concluded from TEM and $CO_2$-TPD experiments. Moreover, the surface barium sulfates reduction is also affected by the pre-treatment. Only one peak is observed near 650 °C after the oxidizing pre-treatment, whereas two peaks were obtained at lower temperature (500 and 600 °C) after the neutral pre-treatment. These results clearly show that the surface sulfates formed on the catalysts treated under nitrogen are less stable than those deposited on the catalysts treated under $O_2/N_2$. According to the literature [23,26], it is explained by a higher Pt-Ba proximity and a higher Ba dispersion for the catalysts treated under $N_2$. This beneficial effect of the $N_2$ pre-treatment before aging is observed whatever the preparation method.
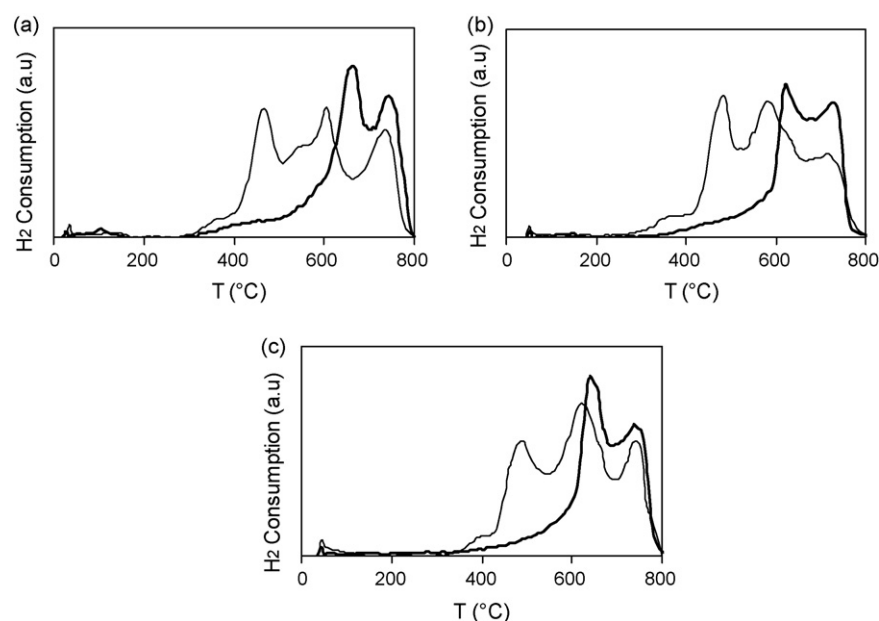


**Fig. 7.** $H_2$-TPR profiles of aged Pt/20Ba/Al catalysts sulfated at 300 °C, prepared by (a) impregnation method, (b) precipitation and (c) co-addition method. Before hydrothermal aging at 700 °C, the catalysts were treated at 700 °C under (−) $N_2$ or (▬) $O_2/N_2$.

### 3.3. Discussion

This study shows the beneficial effect of a $N_2$ pre-treatment at 700 °C (compared to a $O_2/N_2$ one) before a hydrothermal aging at the same temperature. Under realistic conditions, with $H_2O$ and $CO_2$ in the feed stream, the rapid NOx storage capacities (100 s) are at least two times higher with the $N_2$ pre-treated catalysts, whatever the storage temperature (200–400 °C) and the catalyst preparation method.

Two main parameters can explain these results: an improvement of the barium dispersion and an improvement of the platinum dispersion.

About the first point, a large number of TEM pictures of the Pt/20Ba/Al samples were analyzed by EDX. Barium component was detected everywhere for the $N_2$ pre-treated samples, whereas barium-free alumina was detected for the $O_2/N_2$ pre-treated catalysts. This result seems to indicate a higher barium dispersion for the $N_2$ pre-treated sample. Nevertheless, this technique is not sufficient to have a confident description of the samples and other characterizations confirm that the pre-treatment atmosphere ($N_2$ or $O_2$) before aging really influences the barium dispersion.

The $CO_2$ desorption results show that, for a same Ba loading, the proportion of bulk barium carbonates really decreased when the catalysts were treated under $N_2$ before aging. As the bulk barium carbonates are related to poorly dispersed Ba species, it can be concluded that the $N_2$ pre-treated catalysts exhibit a higher Ba dispersion than those pre-treated under $O_2/N_2$ before aging.

These results are corroborated with the TPR profiles of the sulfated samples. The bulk barium sulfates amount (reduction peak near 750 °C, corresponding to large Ba species) is lower when the catalysts are pre-treated under $N_2$. Moreover, long time storage tests (900 s) indicate an increase of the total number of the storage sites using the $N_2$ pre-treatment, even if some small nitrate diffusion into the large barium particles cannot be totally excluded. Finally, all these characterizations led to the same conclusion: the $N_2$ pre-treatment before aging improves the Ba dispersion, compared to the $O_2/N_2$ pre-treatment. As a consequence, the basic strength of the storage material pre-treated under $N_2$ is lower and it induces a lower inhibiting effect of $CO_2$ and $H_2O$ during the storage tests.

Nevertheless, the TPD experiments of the $N_2$ pre-treated catalysts do not exhibit a two times higher "surface" $CO_2$ desorption (compared to the $O_2/N_2$ pre-treated catalysts), which would explain two times higher rapid NOx storage capacities. However, platinum should not play a critical role for the $CO_2$-TPD experiments, in opposition with the NOx storage tests, especially for the rapid storage. Then, the influence of the pre-treatment atmosphere on the platinum properties was examined.

The platinum dispersion of the aged Pt/20Ba/Al catalysts, deduced from $H_2$ chemisorptions and TEM measurements, increases from about 4–5 to 8–9% for the $O_2/N_2$ and $N_2$ pre-treatments, respectively. Even if the platinum particles are still large in both cases, it means that the number of particles increases of practically one order of magnitude when the catalyst is pre-treated under $N_2$ before aging. Furthermore, some TPR experiments under hydrogen indicate that the platinum particles are also in a more metallic state when the aged catalysts were pre-treated under $N_2$. The increase of both platinum dispersion and the metallic state explain the increase of the NO oxidation activity.

In conclusion, both platinum and barium are more dispersed on the aged catalysts pre-treated under $N_2$, leading to an improvement of the Pt-Ba proximity. These results are supported by the TPR characterizations of the sulfated samples. Whatever the preparation method used, the $N_2$ pre-treated catalysts exhibit a larger amount of surface barium sulfates related to a higher barium dispersion, and a weaker stability, resulting from a better Pt-Ba proximity. Note also that the $N_2$ pre-treatment effect on the NOx storage properties of the aged catalysts remains after sulfating and sulfur regeneration in rich mixture.

## 4. Conclusion

In the present work, the influence of the pre-treatment atmosphere ($O_2/N_2$ or $N_2$) at 700 °C before aging at the same temperature under wet air was investigated on Pt/Ba/Al model catalysts. Two barium loadings were studied, 10 and 20 wt%, respectively. The catalysts were prepared by platinum impregnation on Ba/Al materials previously calcined at 700 °C or by co-addition of Pt and Ba. For the Ba/Al materials, barium was deposited by impregnation or precipitation. The preparation method has a low impact on the rapid NOx storage. On the contrary, the pre-treatment of the catalysts under $N_2$ before aging leads to higher NOx storage properties than the catalysts pre-treated under $O_2/N_2$. The difference is even more significant when the NOx storage capacity is measured in the presence of $H_2O$ and $CO_2$ ($\times 2.04$ and $\times 2.40$ for 10 and 20% BaO content, respectively). The nitrogen pre-treatment before the thermal aging induces:

(i) a higher dispersion of platinum.
(ii) a greater barium dispersion, thus leading to a higher number of active Ba sites for the NOx storage. This effect is more significant for the 20 wt% BaO catalyst than for the 10 wt% BaO one because barium is already quite stabilized for the low barium content.
(iii) a better Pt-Ba proximity, which leads not only to an increase of the rapid NOx storage but also to the formation of less stable sulfates.

In conclusion, the pre-treatment of model Pt/Ba/Al catalysts under inert atmosphere at 700 °C improves both the oxidation and the storage functions, leading to more durable NOx storage catalysts. It is remarkable that this effect is observed after a quite severe hydrothermal treatment at 700 °C.

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